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㉒ Apparatus for removing sulfur from organic polysulfides.

㉓ Sulfur-laden liquid organic phase dimethyl polysulfide (DMPS) is caused to rise from a sour gas well by reaction of the gaseous sulfur component within the well with a sulfur solvent, typically dimethyl disulfide (DMDS). The DMPS is contacted by an extraction or stripping liquid in a vertical column continuous multistage countercurrent flow extractor especially designed to promote high interfacial area contact between the liquids while flowing in opposing directions within the column.

**EP 0 267 471 A1**

# APPARATUS FOR REMOVING SULFUR FROM ORGANIC POLYSULFIDES

## CROSS-REFERENCE TO OTHER APPLICATIONS

Reference is made herein to application Ser. No. 878,163, filed June 25, 1988, of Yen et al., for "Process for Removing Sulfur from Organic Polysulfides", and assigned to the present assignee.

## Statement of the Invention

This invention relates to the removal of sulfur from dimethyl polysulfides (DMPS) formed by the reaction of  $H_2S$ , for example, contained within a sour gas well, with a sulfur solvent, typically dimethyl disulfide (DMDS), pumped into the well, and more particularly to an improved extractor for removing said sulfur efficiently and economically.

## Background and Summary of the Invention

Sulfur deposition in downhole tubular and wellhead equipment associated with sour gas wells is usually troublesome to sour gas producers. Elemental sulfur,  $H_2S$ , and polysulfides are the principal sources of these unwanted sulfur deposits.

Dialkyl disulfides, alkyl disulfides and polysulfides, and particularly dimethyl disulfide (DMDS),  $CH_3SSCH_3$ , are effective sulfur-dissolving agents or solvents for cleaning sulfur deposits. The relatively low flammability and vapor pressure of DMDS make it very attractive as a sulfur-dissolving solvent in sour gas wells. Further, DMDS can be efficiently regenerated through chemical wash. In the present application and aforementioned cross-referenced patent application, DMDS is regenerated in a multistage continuous countercurrent flow extractor.

Many processes in the prior art are known for the extraction of dissolved sulfur from solvents. For example, in U.S. Patents numbered 3,474,028, 3,489,877, 3,617,529, 3,748,827, 4,018,572, and 4,230,184, the use of alkali metal and ammonium hydrosulfides and sulfides to remove dissolved sulfur from mineral oils are disclosed. The publication of Dowling, Lesage, and Hyne for Regeneration of Loaded Dimethyl Disulfide Based Sulfur Solvents, Alberta Sulfur Research Limited Quarterly Bulletin, Vol. XXI, Nos. 3 & 4, pp.30-52, October 1984 - March 1985, discloses the regeneration of dimethyl disulfide by stripping sulfur from dimethyl polysulfide (DMPS) in a batch operation with alkali metal and ammonium hydrosulfides and sulfides, preferably sodium sulfide. None of the above prior art references discloses or suggests however the instant continuous multistage countercurrent flow extraction apparatus for removing sulfur from organic polysulfides.

The extractor apparatus of the present invention comprises a vertical multistage column extractor or reactor containing a distributor means at each end thereof, each of the stages comprising a packing section; a pair of redistributor plates with an agitator therebetween, each of the above recited components being spaced from each other, as well as from the packing section of an adjacent stage. A final packing section is provided adjacent that distributor means devoid of one adjacent thereto such that a packing section is disposed interiorly each distributor means.

The arrangement of components within the extractor and within each stage thereof insures efficient countercurrent flow of the two immiscible liquids, i.e., the stripping or extraction solution, typically aqueous  $Na_2S$ , and the sulfur-laden liquid organic phase (DMPS), such that high interfacial area contact is constantly maintained between the liquids.

## Brief Description of the Drawings

FIG. 1 is a flow diagram illustrating a process for removing sulfur from a dialkyl polysulfide formed within a sour gas well, the process employing the improved extractor apparatus of the present invention.

FIG. 2 diagrammatically illustrates a vertical section through the extractor of the present invention.

FIG. 3 is a flow diagram illustrating a process using a series of continuous stirring tank reactors (CSTR) and separators for removal of sulfur from DMPS.

Reactor tanks 301, 305, 309 and 313 may conveniently comprise conventional continuous stirring tank reactors (CSTR).

Among the sulfide salts and/or hydrosulfide salts suitable for use in the present invention, sodium sulfide in water is preferred, preferably at a concentration of between 10 weight percent and the saturation concentration of sodium sulfide at the operating temperature of the system.

The preferred reaction times (defined as the total liquid volume flow rate of the organic and aqueous phases divided by the sum of the available reaction volumes in the reactors) range from 5 to 120 minutes; generally the operation is complete in 30 minutes. At contact times shorter than 5 minutes regeneration is insufficient while contact times longer than 120 minutes do not result in significantly improved regeneration.

The molar ratio of the sulfide salt and/or hydrosulfide salt in the aqueous solution to the recoverable sulfur in the organic polysulfide (R value) may range from 0.10 to 0.70; the preferred range is 0.20 to 0.40. Using R values below 0.10 result in incomplete regeneration while using R values above 0.70 result in decreased recovery of the organic polysulfide.

The organic polysulfide need not necessarily originate from the downhole cleaning of a sour gas well. In the preparation of lower organic disulfides, the disulfides are frequently separated from their co-produced polysulfides by distillation. However, it is often not feasible to purify higher organic disulfides (e.g., butyl, hexyl, nonyl, etc.) by distillation because of decomposition and the apparatus of this invention can be employed to produce higher organic disulfides from their respective polysulfides.

#### Example

Employing the system of FIG. 3, dimethyl polysulfide containing 25.9 weight % recoverable sulfur was reacted with a 17% aqueous solution of sodium sulfide in a continuous, countercurrent flow, direct contact two-stage system for a total of 5 minutes in the system. The molar ratio of the sodium sulfide to recoverable sulfur was 0.30. Values of 81% regeneration of the organic dimethyl disulfide and 92% recovery of the dimethyl disulfide were obtained.

For purposes of comparison, the same experiment was repeated except that a continuous single stage system was used in place of the multi-stage, countercurrent flow, direct contact system. The molar ratio of sodium sulfide to recoverable sulfur for this experiment was 0.40. Values of 61% regeneration of the organic dimethyl disulfide and 90% recovery of the dimethyl disulfide were obtained. Thus, the countercurrent, multi-stage technique of the present invention results in a savings of 25% of sodium sulfide over a single stage system.

Percent regeneration and percent recovery are redefined as follows:

$$\% \text{ Regeneration} = \frac{\text{wt \% } S_R \text{ (in)} - \text{wt \% } S_R \text{ (out)}}{\text{wt \% } S_R \text{ (in)}} \times 100$$

$$\% \text{ Recovery} = \frac{\text{wt Disulfide (in)}}{\text{wt Disulfide (out)}} \times 100$$

where  $S_R$  is the sulfur that has been chemically incorporated into the organic polysulfide.

#### Claims

1. A multistage continuous countercurrent flow extractor for removing sulfur from an organic polysulfide of high sulfur rank comprising a vertical column having a heavier liquid inlet at a first end and lighter liquid inlet at a second end, said first end having an outlet for said lighter liquid after traversing upwardly the length of said column and said second end having an outlet for said heavier liquid after traversing downwardly the length of said column, said liquids being immiscible, said column containing a plurality of successive similar stages disposed longitudinally therein, each of said stages including components spaced from each other and from adjacent stage, each of said stages sequentially comprising,

a packing section,  
 first redistributor means,  
 agitating means, and  
 a second redistributor means,

- 5 distributor means interiorly adjacent said first and second ends for uniformly dispersing inwardly said heavier and lighter liquids respectively, and  
 a final packing section adjacent said distributor means devoid of a packing section adjacent thereto.

2. Apparatus of claim 1 wherein said organic polysulfide and heavier liquid is dimethyl polysulfide (DMPS) and said lighter liquid is an extracting or stripping solution comprising aqueous sodium sulfide.

- 10 3. Apparatus of claim 2 wherein said aqueous sodium sulfide extracts sulfur from said DMPS as each of said liquids travels countercurrently to the other within said column to form an aqueous phase of increased sulfur content and a polysulfide of lower sulfur rank.

4. Apparatus of claim 3 wherein said packing sections assist in providing high interfacial area contact between said liquids while traversing countercurrently in said column.

- 15 5. Apparatus of claim 4 wherein said agitating means rotates at a speed adapted to augment said high interfacial area contact and to maintain the countercurrent directions of flow of the respective liquids.

6. Apparatus of claim 5 wherein said packing sections comprise Raschig Rings.

7. Apparatus of claim 5 wherein said packing sections comprise Pall Rings.

8. Apparatus of claim 5 wherein said packing sections comprise saddles.

- 20 9. Apparatus of claim 5 wherein said packing sections comprise mesh screens.

10. Apparatus of claim 5 wherein said packing sections comprise grid packing.

11. Apparatus of claim 5 wherein said redistributor means comprise circular plates having spaced orifices therethrough.

12. Apparatus of claim 5 wherein said liquid exiting said outlet at said first end of said column is  
 25 dimethyl disulfide.

13. Apparatus of claim 1 wherein said lighter liquid is said organic polysulfide and said heavier liquid is an extracting or stripping solution of aqueous sodium sulfide.

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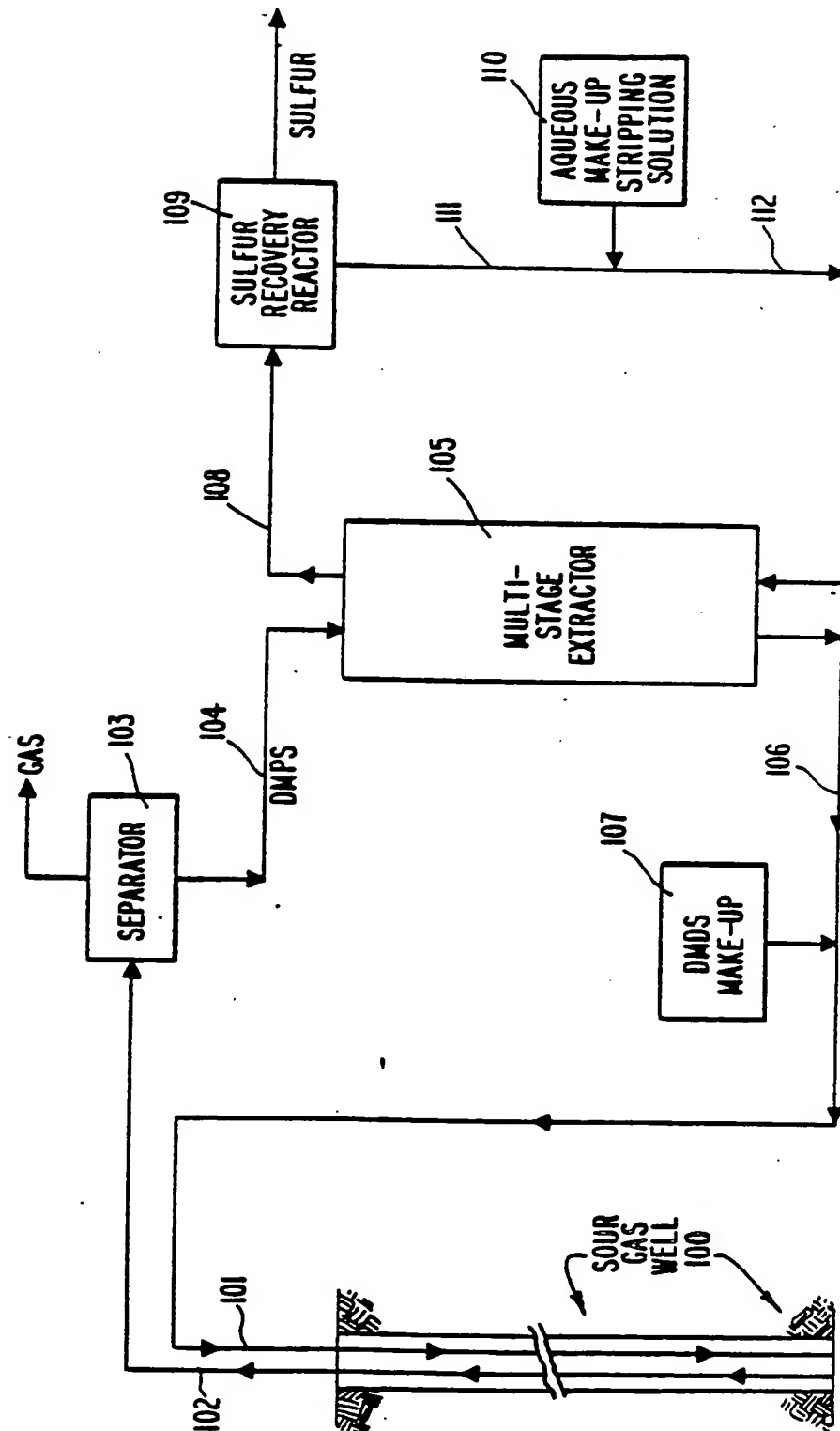
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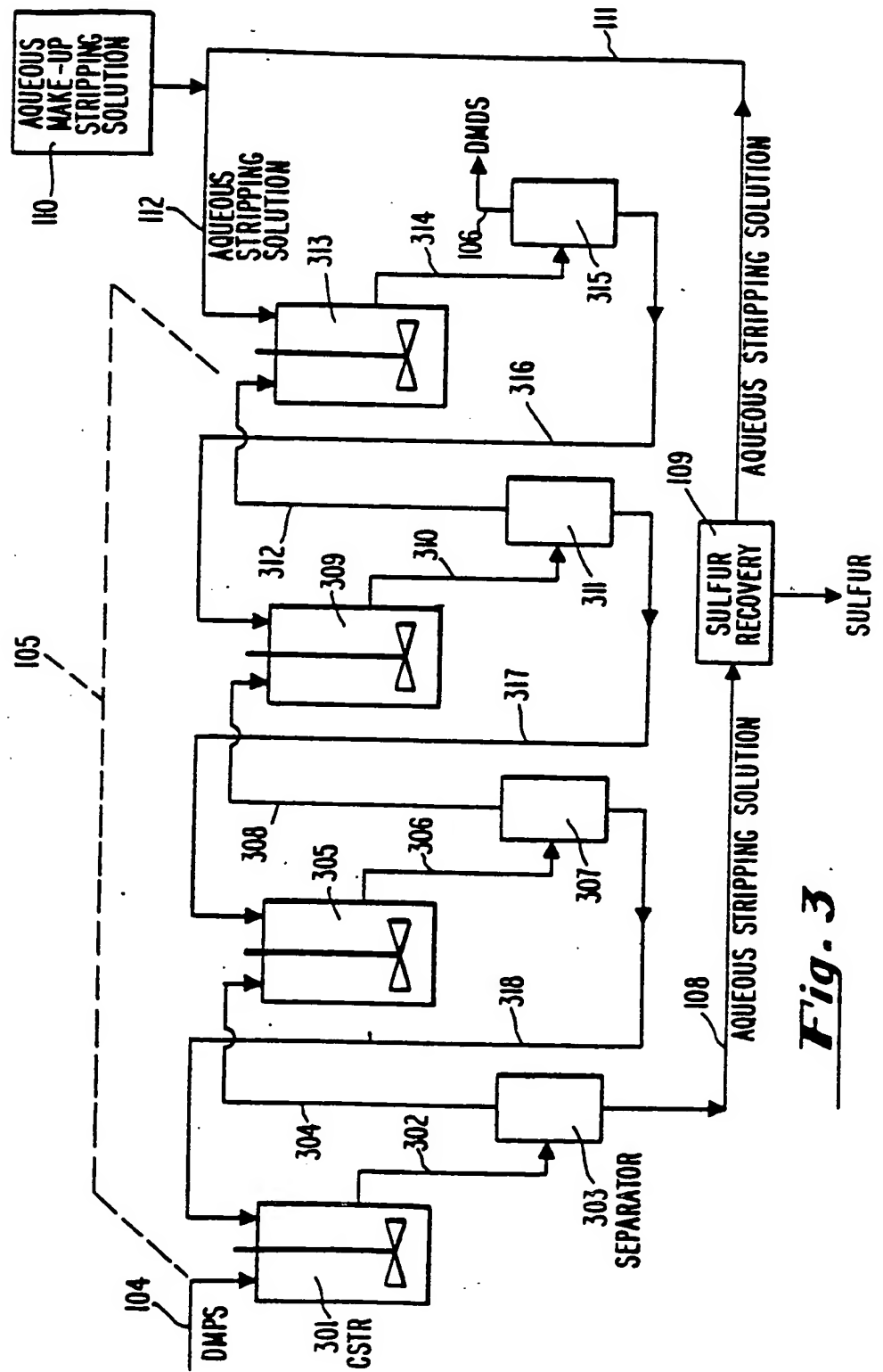
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**Fig. 1**

**Fig. 3**